



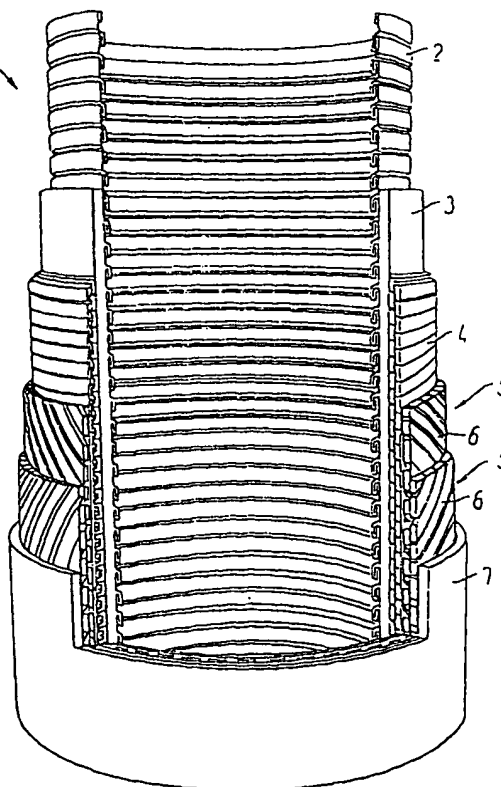
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: UNBONDED FLEXIBLE PIPES AND METHOD FOR THE PRODUCTION THEREOF

## (57) Abstract

The invention relates to a flexible, unbonded continuous high-pressure pipe comprised of several layers comprising at least one inner barrier layer, at least one tubular, liquid-permeable reinforcement layer surrounding the barrier layer, and a tubular outer sheath surrounding the tubular reinforcement layer(s), wherein at least one liquid-impervious barrier layer is provided by continuous extrusion of a single-phase aliphatic polyketone polymer, and a method for the production thereof.



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Unbonded flexible pipes and method for the production thereof

5 The present invention relates to a flexible, high-pressure and high-temperature pipe which is particularly suitable for the transportation of oil/gas (or hydrocarbons) in connection with oil production in offshore fields and to other transportation of oil/gas, and to a method for the production of such flexible  
10 pipes.

In the transportation of oil and gas products, a combination of more or less complex demands have to be met, as the transportation often takes place over long  
15 distances and at high temperatures, and between localities which may be mutually movable, e.g. ship and platform or bottom and floating platform. The pipes used in this connection should therefore meet complex demands of different types as will appear from below.

20 The pipes may be very long, often several kilometers. At the same time they should possess a sufficient degree of flexibility for allowing them to be wound into coils and onto revolving platforms in order that they may be  
25 transported to their site of use. The pipes should be able to stand being wound into and unwound from the coils and revolving platforms at temperatures of typically down to -20 °C, and further be able to tolerate at least up to 100 °C, preferably up to 150 °C, during oil  
30 transportation and the like. A further demand placed on the pipes is their capability for standing mechanical stress, such as high pressures, e.g. a pressure of more than 10 mPa (100 bars), pressure variations, tensile forces caused by the conditions below the sea surface.  
35 Further they should possess good barrier properties to both oil/gas (or hydrocarbons) and sea water.

The life of flexible pipes of this type should typically amount to 20 years without any risk of oil spill. The risk of pollution due to leakage is completely unacceptable, and it is therefore imperative that the pipes are flawless when put into use.

Flexible pipes for the application mentioned above are described in e.g. EP-B1-0487691 and WO 96/30687.

10

A flexible pipe of the above mentioned type may e.g. comprise an inner flexible metal cylinder. The design of said cylinder may vary, and one example thereof comprises a metal carcass, the purpose of which is mainly to provide the pipe with the necessary mechanical strength against collapse, including ensuring that the cross section of the pipe remains the same irrespective of any external impact exerted on the pipe. As used herein carcass means mutually engaging profiled metal bands. Said bands ensure proper flexibility of the pipe. This inner, flexible, liquid-permeable cylindrical metal body may also have other forms, e.g. the form of a corrugated metal pipe. The inner diameter of such pipe will normally be up to e.g. 50.8 cm (20 inches).

25

Round the metal carcass is typically a barrier layer consisting of a plastics material, the purpose of which is to provide the pipe with the necessary barrier properties against the product to be transported in the pipes. Optionally there may be several such barrier layers.

In addition, a typical pipe comprises a number of reinforcement layers, e.g. consisting of metal bands or wires wound in helical form with e.g. a C-profile and a rise of 80-90°, rendering the pipe resistant to radial

35

pressure and at the same time providing the pipe with a high degree of flexibility. As used herein rise means the angle between the longitudinal axis of the metal band and the longitudinal axis of the pipe.

5

The second layer, which e.g. may be comprised of a flat or a round metal wire wound in helical form with a rise of about 35°, provides the pipe with the necessary tensile strength. Typically two layers are involved,  
10 wound in opposite directions in order to equalize the torsional forces.

In order to ensure movability of the metal layers relative to each other, one or more winding layers may be  
15 provided between said metal layers.

Finally, the outer layer may comprise an outer sheath consisting of extruded thermoplastics, e.g. polyethylene or polyamide for protection against penetration of sea  
20 water with possible resultant corrosion.

All these layers are typically assembled at each end of the pipe in an endfitting made from e.g. carbon steel, to which each of the above mentioned layers is secured.

25

As already mentioned above, a finished flexible pipe may often be very long and be provided with an endfitting at each end, but due to its flexible structure it may be wound onto large revolving platforms or coils, which  
30 facilitates handling significantly.

In the prior art pipes of the above mentioned type, the barrier layer is typically produced by extrusion of polymers, such as polyethylene (PE), polyamide (PA) or  
35 polyvinylidene fluoride (PVDF).

However, pipes, in which the inner barrier layer is made of these polymers, have some significant shortcomings, as the polymer materials do not live up to the requirements outlined above.

5 Polyethylene (PE) thus has limited barrier properties to gases which typically are present in crude oil and natural gas deposits, including in particular carbon dioxide, methane and hydrogen sulphide. This means in practice that these gases can migrate through the sealing  
10 layer out to the metal reinforcement elements, where they may cause corrosion (as regards carbon dioxide and hydrogen sulphide) or build-up of an undesired high pressure. An undesired high pressure at the metal reinforcement elements can result in disruption of the  
15 outer sheath with resultant penetration of sea water, which thereafter will lead to corrosion of the reinforcement elements.

It is an additional limitation to the use of PE that flexible pipes with barrier layers of this material can  
20 be used only at relatively low temperatures of up to about 60 °C.

Of polyamides, usually polyamide-11 or polyamide-12 is used, which have good resistance to crude oil, whereas at high temperatures they tend to undergo undesired  
25 hydrolysis in the presence of water. In case of offshore applications the water content may increase during the life of the field, and thereby the barrier layer is gradually exposed to water at such an elevated temperature. The amide bonds are consequently hydrolyzed  
30 with resultant decomposition of polymer chains, which results in a considerable reduction of the mechanical strength.

The polyamides also have an undesired high permeability to various gases and liquids, such as e.g. methane, carbon dioxide, hydrogen sulphide, and water. In particular it should be mentioned that even a minor  
5 degree of hydrolysis may result in a higher permeability, whereby the above gases and liquids can migrate faster through the barrier layer out to the metal reinforcement elements, which may give rise to corrosion or build-up of an undesired high pressure, as mentioned earlier, which  
10 may cause mechanical rupture in the reinforcement elements. As a result, the life of the pipe is reduced to an unacceptable level.

Barrier layers consisting of PVDF have good barrier properties to both the above gases and liquids, whereas  
15 PVDF is extremely difficult to process.

In a pure state, the PVDF material is comparatively notch sensitive, meaning tendency to disrupt when exposed to impacts near an incision or a notch shaped recess in the material. This phenomenon especially arises in case of  
20 brittle materials, and as regards polymer materials the notch sensitivity is particularly high at temperatures significantly below the glass transition temperature  $T_g$  of the polymer material. Notch sensitivity can e.g. be measured by the so-called Izod impact resistance test  
25 according to ASTM D256. The higher energy required for forming a crack, the smaller notch sensitivity.

A low molecular plasticizer is consequently often added to PVDF, which makes the material more easy to process and reduces the notch sensitivity. A much used  
30 plasticizer is dibutyl sebacate (DBS). However, this plasticizer can migrate out and thereby result in undesired changes in the properties of the barrier layer,

such as a more rigid material, and changed dimensions due to volume reduction.

Prior art flexible pipes comprising barrier layers of the above-mentioned plastics types, of course, all have  
5 different limitations and hence limited possibilities of use.

Thus, the object of the present invention is to provide flexible pipes which are particularly well suited for the transportation of oil and gas products, in particular  
10 pipes which do not suffer from the drawbacks in use or in life associated with the prior art pipes.

A particular object of the present invention is to provide long-life, flexible pipes which further comprise barrier layers with a particularly low notch sensitivity,  
15 said barrier layer being provided by one-piece extrusion.

A further object of the present invention is to provide flexible pipes with good thermo-insulating properties, ensuring that the major part of the temperature drop takes place above the barrier layer, thereby resulting in  
20 a low temperature in the reinforcement layer. This reduces the diffusion rate and hence the corrosion rate and generates a smaller gas pressure.

Furthermore, it is the object of the present invention to provide flexible pipes having a barrier layer with a  
25 particularly low solubility to gases. Thus no gas pockets or blisters are formed by the gas in case of a sudden decompression during abnormal operation. This is considered good blister properties.

Furthermore, it is the object of the present invention to  
30 provide flexible pipes having a barrier layer with a particularly low permeability to gases, in particular H<sub>2</sub>S

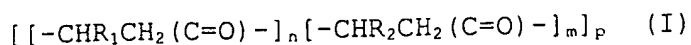


and CO<sub>2</sub>, in order to reduce corrosion of the reinforcement layer.

These objects are achieved by the flexible pipe according to the invention, as recited in claim 1.

- 5 As used herein unbonded means that the individual layers are not bonded together and therefore are allowed to slide relative to each other in the longitudinal direction of the pipe.

Flexible pipes according to the invention comprise at least one inner barrier layer comprising aliphatic polyketones having the general formula I:



- where R<sub>1</sub> og R<sub>2</sub> are mutually different and independently mean hydrogen or an alkyl group, preferably methyl-, ethyl-, propyl-, pentyl-, or heptyl-, and n + m = 1, where n is preferably less than 0.5, more preferably between 0.02 and 0.8, and p is an integer, preferably an integer between 500 and 5000, and where the two comonomers are randomly distributed or blocked. The pipes of the invention have been found to be particularly suitable for transportation of oil and gas products.

- The flexible pipes of the invention may comprise several barrier layers, of which at least one comprises an aliphatic polyketone as defined above. The other layers, if any, may be of the same material or they may be constituted by some of the above-mentioned PE, PA, or PVDF types. An inner layer of PE can e.g. provide a smooth surface in the extrusion of the polyketone and at the same time reduce the costs of the product. Furthermore, three barrier layers may be provided, of

which e.g. the middle layer may consist of polyketone, whereas the two other layers may be made of PE.

The barrier layer comprising aliphatic polyketones (in the following simply referred to as the barrier layer) has a very low permeability to CH<sub>4</sub> and CO<sub>2</sub> and thus provides a good barrier to oil and gases. A technical documentation by Shell Chemicals (Carilon Polymers Oil and Gas Applications, Shell Chemicals SC:2643-98, 09/21/98) compares gas permeability of CH<sub>4</sub>, H<sub>2</sub>S and CO<sub>2</sub> through an aliphatic polyketone with the permeability through HDPE and PA-11. The permeability through PA-11 is about twice as high as through the polyketone, whereas the permeability through HDPE is 5 to 10 times higher than through the polyketone. In terms of barrier properties, the aliphatic polyketone is thus better than PA-11 and HDPE. In addition, the barrier layer has a high mechanical strength and is resistant to bending and stretching.

The good barrier properties reduce the problems associated with stress corrosion (e.g. SSIC - Sulfide Stress Induced Cracking) and hydrogen induced cracking (HIC), thus allowing use of high-tensile steel for reinforcement.

Moreover, the flexible pipes of the invention have a substantiated chemical resistancy, as the barrier layer has been found to be highly insensitive to hydrolysis, meaning that no problems arise even in case of a high content of water in the oil and gas products. Besides, the barrier layer does not swell when contacted with hydrocarbons.

In addition, the barrier layer has a low solubility to gases, thus avoiding the formation of blisters in connection with a sudden decompression.

5 It has been found that aliphatic polyketones as a material group have a low notch sensitivity and may be processed without the addition of a plasticizer. As mentioned in e.g. WO 98/14513, a plasticizer may, however, be added provided that the plasticizer is not of a low molecular type and that the addition thereof does  
10 not result in any undesired changes in the mechanical properties of the barrier layer.

It is preferred to use a continuous flexible pipe according to the invention for the transportation of oil/gas under high pressure and for offshore use, e.g.  
15 below the sea surface, i.e. a pipe often of a length of at least 50 meters, which typically comprises a number of different layers.

Fig. 1 illustrates the structure of an embodiment of an unbonded flexible pipe according to the invention.

20 The flexible pipe 1 shown in Fig. 1 comprises an inner metal cylinder (2) which serves to ensure the necessary mechanical strength and flexibility of the pipe. As shown in Fig. 1, this metal cylinder is provided by the winding-up in a helical form with a slight rise of a  
25 metal band, preferably of stainless steel, the cross section of which has an Z or an S shape. The metal cylinder may also have other forms, e.g. that of a corrugated pipe. It should be emphasized that this layer is not imperative for the structure of the pipe according  
30 to the invention, and thus it may be excluded in other embodiments.

The layer (3) is an inner liquid-impervious barrier layer provided by continuous extrusion of a single-phase aliphatic polyketone polymer as recited in claim 1. The purpose of this layer is to provide the pipe with the necessary impermeability to the product to be transported in the pipe. Preferably the layer has a thickness of 5 to 12 mm. Optionally several layers of the same material may be used.

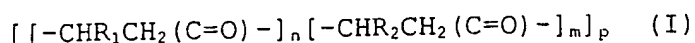
The layer (4) is a reinforcement layer consisting of a metal band wound in a helical pattern, preferably with a C-profile, said layer providing resistance to radial pressure and at the same providing suitable flexibility. Other cross-section may also be used.

The tensile reinforcement layers (5) each consists of a number of metal wires (6) wound in a helical pattern, in said case of a rectangular cross-section, but metal wires of other cross-sections may also be used. In order to render the pipe torsion free, the two layers are wound in opposite directions.

The outer layer (7) is a sheath which serves to protect the flexible pipe against penetration of sea water and against damage related to the laying out of the pipe. The layer is typically provided by extrusion of a thermoplastics. The pipe typically has a diameter, calculated as the inner diameter of the metal carcass - or in embodiments with no such metal carcass - calculated as the inner diameter of the barrier layer, of at least 5 cm, preferably at least 15 cm.

Thus, the flexible pipe according to the invention comprises an inner liquid-impervious barrier layer. This barrier layer is usually extruded in one piece. In particular it is preferred that the polymer material used is a single-phase polymer material comprising 90% by

volume or more, preferably at least 95 % by volume, of an aliphatic polyketone having the formula (I)



wherein  $R_1$  and  $R_2$  have the meanings defined above.

- 5 Preferred compounds are those wherein  $R_1$  is  $\text{CH}_3$ ,  $R_2$  is H, and  $n$  is less than 0.10, preferably between 0.02 and 0.08, or wherein  $R_1$  is alkyl,  $R_2$  is H, and  $n$  is less than 0.10, and  $p$  is an integer between 500 and 5000, and where  
10 the two comonomerss are randomly distributed. However, it is particularly preferred that  $n = 0$ , and  $R_2$  is H, or that  $R_1$  is  $\text{CH}_3$  and  $R_2$  is H.

A suitable polymer material comprises Carilon® terpolymer, wherein  $R_1$  is  $\text{CH}_3$ , and  $R_2$  is H,  $n$  is about 0.05 and  $m$  is about 0.95, and  $p$  is between 500 and 5000  
15 (sold by Shell Chemical Company). A brochure issued by Shell (Carilon® Thermoplastic Polymers) states that these materials are suitable for all kinds of processing, such as injection moulding, blow moulding, rotational casting and extrusion. It further mentions that the  
20 materials can be used for fibres, films, coatings, package materials, pipe pieces and more, as normally described in such sales brochures. It further mentions that these materials are suitable for automatic fuel systems. Carilon® polymer materials are said to have  
25 good barrier properties to fuels and their fumes.

Now it has surprisingly been found that a single-phase aliphatic polyketone polymer as recited in claim 1 can be used for the liquid-impervious barrier layer in flexible unbonded, continuous pipes for high-pressure use.

- 30 Thus, it has surprisingly been found that single-phase aliphatic polyketone polymers when used as liquid-

impervious barrier layers in flexible pipes according to the invention can stand being bent and stretched at temperatures down to typically -20 °C and up to about 100 °C, and that the notch sensitivity of the materials in  
5 such use is satisfactorily low.

Furthermore, a flexible pipe according to the invention having a barrier layer of such single-phase aliphatic polyketone polymer has been found to exhibit particularly good thermo-insulating properties, and such flexible pipe  
10 has also been found to enjoy good blister properties. Further, this material exhibits a particularly low permeability to H<sub>2</sub>S and CO<sub>2</sub>, meaning that flexible pipes according to the invention having a barrier layer consisting of a single-phase aliphatic polyketone polymer  
15 and metal reinforcements as explained above enjoy a particularly high protection against corrosion.

However, a particular important property exhibited by the single-phase aliphatic polyketone polymer is that it can be extruded continuously without disruptions and hence  
20 without formation of stiff or weak areas in the material. This allows production of long lengths of flexible unbonded pipes. As used herein "long lengths" mean tubular lengths of at least 50 meters, preferably of at least 200 meters.

25 The liquid-impervious barrier layer typically has a thickness of 5 to 12 mm, preferably of 6 to 10 mm. In case of flexible pipes without a tubular inner metal cylinder, it is, however, recommendable to use a thicker barrier layer, e.g. of up to 20 mm, as the pipe will  
30 otherwise collapse in connection with bending and winding-up.

Another suitable polymer material comprises Ketonex terpolymer, test marketed by General Electric Plastics in

cooperation with BP Chemicals. The chemical composition is substantially as the one described above.

Besides, it is the object of the invention to provide a method for the production of the above mentioned flexible  
5 pipes.

As far as the pipe type of the present invention is concerned, it is of utmost importance that extrusion can be effected continuously for a prolonged period of time, as assembly of pipe pieces with endfittings in other  
10 places of a pipe section than by its ends should be avoided. Such endfittings are costly and further contribute to a more stiff pipe section. Pipe sections with endfittings provided in other places than by their ends thus result in a comparatively stiff pipe section,  
15 which is difficult to handle.

Besides, it is of utmost importance that the extrusion can be effected in a continuous process and without any significant disruptions for a prolonged period of time, as pipes for use in the transportation of oil and the  
20 like require that the flexible pipe section contains no assemblies of barrier layers. As mentioned above, it is also important that the barrier layer in the pipe is in perfect condition, as repair work on the layer is not possible.

25 It has now been found that the method according to the invention, as recited in claim 14, provides such a continuous extrusion for obtaining the desired pipe type in lengths of at least 50 meters.

Surprisingly it has been found that extrusion of  
30 aliphatic polyketones with the formula (I) at a temperature close to that of their melting point produces a barrier layer with particularly good properties.

In a conventional extrusion process, the polymer will typically be heated to a temperature far above that of its melting point in order to lower the viscosity of the melt. As far as aliphatic polyketones are concerned, it has been found that the polymer, due to its cross-binding (presumably by the so-called aldol condensation wherein two polymer chains react and form a beta hydroxyketone which again react by water separation so as to form a carbon-carbon double binding), as a result of a too high temperature and an excessive retention time produces an increased viscosity, which again results in an increased viscous energy metabolism in the polymer, causing the cross-binding to be self-reinforcing. In zones of the processing equipment where the flow is particularly slow, the melt may not move at all, said zones being referred to as dead zones. In said zones an increasing decomposition of the material gradually takes place, and the result thereof is often that the production has to be suspended after a short period in order to allow cleaning of the equipment. This short operation time does not allow production of long lengths of flexible pipes.

For numerous pipe types, e.g. pipes of modest length and thickness, this does not constitute a problem, and thus use of this type of polymer in the production of thin pipes or co-extruded pipes intended for e.g. gasoline tubings in cars, is known from e.g. US 5,232,786 and JP 10002258 A.

Thus, it has previously not been known to use polyketones for the production of flexible pipes of the type defined in the application for the transportation of oil and gas products.

However, use of the method according to the present invention, as recited in claim 14, avoids these problems.



Efficient control of the temperature conditions in the processing equipment thus prevents said dominant decomposition mechanism (aldol condensation).

Thus, several, closely nabouring double bindings result  
5 in a product without heavily branched chains and without any discolouring, which would otherwise be expected in connection with a conventional processing process.

The method according to the invention for the production of a flexible, unbonded high-pressure pipe optionally  
10 comprises the provision of a metal carcass followed by the provision of a liquid-impervious barrier layer by continuous extrusion, a subsequent reinforcement with at least one layer of metal band, the provision of a liquid-impervious, tubular outer sheath, and the assembly of the  
15 provided tubular parts, and the sealing of said parts in an endfitting.

The liquid-impervious barrier layer is produced according to the invention by continuous extrusion of a single-phase aliphatic polyketone comprising at least 80% by  
20 volume of an aliphatic polyketone as recited in claim 1, which provides a barrier layer with particularly good properties in terms of i.a. thermal insulation, notch sensitivity, blister and diffusion resistance to gases, such as  $H_2S$  and  $CO_2$ .

Thus, the method of the invention provides a flexible,  
25 unbonded pipe which is particularly suitable for the transportation of crude oil and the like, as already described above. The method further excels in being fast, free of undesired operational stops, without unnecessary  
30 product waste and hence ecomomically acceptable.

In case the unbonded flexible pipe comprises an internal metal carcass preferably made from stainless steel, the

liquid-impervious barrier layer is extruded directly onto the exterior surface of said layer, however preferably onto a winding on said metal carcass. Such winding serves the purpose of allowing the metal carcass and the barrier layer to slide relative to each other during bending in  
5 connection with winding-up, laying out, and operation.

The extrusion equipment used in the method according to the invention comprises a distributor, a pipe head, and an extruder.

10 The temperature and flow is controlled in such manner that the mean temperature of the polymer in the distributor and pipe head does not exceed the melting point of the polymer by more than 15 °C, and the mean retention time of the polymer in the extruder,  
15 distributor, and pipe head does not exceed 20 minutes, while the local temperature of the polymer does not exceed the melting point of the polymer by more than 35 °C for a maximum of 5 minutes. Such control prevents unintended decomposition of the polymer material, thereby  
20 resulting in a barrier layer with the desired properties.

In order to obtain this positive result, the mean retention time of the polymer should not exceed 10 minutes. Likewise, the maximum retention time of the polymer in the extruder should not exceed 3 times the  
25 mean retention time.

Besides, for controlling said proces it is preferred that the extruder have at least 7 heating zones defined by the number of heating bands on the extruder with separate adjustment, and that the temperature in said heating  
30 zones be increasing or constant from inlet to outlet.

In addition it is also preferred that the distributor and cross-head be adjusted by at least 5 heating zones, and

the temperature in said zones should not deviate by more than 5 °C from the temperature set on the extruder.

The invention will now be explained in further detail by way of the following examples which in no way are considered to limit the scope of the invention.

#### Example 1

In a full-scale production plant, a 15.25 cm (6 inches) metal carcass consisting of a folded metal band formed as an S-profile is coated with a layer of an aliphatic polyketone. The outer diameter of said carcass is about 167 mm. For extrusion use is made of an aliphatic polyketone composed of an E/P/CO terpolymer, i.e.  $R_1$  is  $CH_3$ ,  $R_2$  is H, and n is about 0.05, and m is about 0.95. Use is made of a so-called Carilon RDP 229® from Shell having a melting point of 220-222 °C.

Extrusion is effected by use of a single worm extruder having a diameter of 120 mm, an L/D ratio of 30, and with a single groove worm. Use is made of a conventional crosshead tool with a heart leaf distributor. The metal carcass is inserted into the center of the crosshead tool. Extrusion is effected at a thickness of about 8 mm at a rate of about 0.5 m/min. The temperature of the extruder is set to 220 °C in the initial zone and 235 °C in all subsequent zones. During the test, the temperature of the melt is stabilized at 235 °C.

Under such conditions extrusion may be effected in a stable manner and with a sufficient melting strength in the extrudant to allow it to maintain its shape around the carcass during cooling. Cooling is effected in a chamber by applying water by means of nozzles.

It is possible to extrude a barrier layer of satisfactory quality in lengths of more than 50 meters.

After more than 3 hours of extrusion, the extruder is disassembled, and no deposits of discoloured (cross-bound) material are found. During the entire extrusion period constant conditions prevailed in terms of power consumption of the worm engine, pressure and temperature, which are characteristics of a stable process. Thus, with the same temperature set it is likely that extrusion can be effected continuously for several days provided the temperature is not increased.

The extruded barrier layer has the same colour all over, which further indicates that no decomposition of the material has taken place.

#### 15 Example 2

A section of approx. 25 cm is cut out of the barrier layer consisting of the aliphatic polyketone of example 1 and removed from the metal carcass. This section is mounted in a rotating holder, and thin samples of a thickness of approx. 1 mm are cut out of the barrier layer by use of a knife. From each sample, a circular section is cut for permeation and diffusion measurements. The "time-lag method" described by James E. Shelby in "Gas Diffusion in Solids and Melts", ASM International, 1996, is applied.

The circular samples having a diameter of approx. 70 mm and a thickness of approx. 0.96 mm are mounted in a flat diffusion cell on a circular, porous, sintered metal support, through which gas may permeate, of a diameter of 60 mm encircled by a ring-formed metal support. This cell consists of two chambers, a primary high-pressure chamber and a secondary low-pressure chamber.

Carbon dioxide applied on the primary side at a moderate pressure of 2.0 MPa is used as permeating gas. The cell is thermostated at 70 °C. As the gas permeates through the polymer, pressure is gradually building up on the secondary side. The effective diffusion diameter is 60 mm. The permeating gas is detected by a pressure valve opening at a pre-set excess pressure of 2.0 kPa, with a secondary chamber volume of 20.9 cm<sup>3</sup>. Thus, with each opening of the valve, 0.33 cm<sup>3</sup> of gas is permeated (at STP conditions).

The valve opens at equilibrium at intervals of 40.8 minutes in average, i.e. the permeability is  $1.36 \times 10^{-4}$  cm<sup>3</sup>/sec. corresponding to a permeability for the material of  $2.4 \times 10^{-8}$  cm<sup>3</sup> cm/cm<sup>2</sup> Bar sec. From a "time-lag" of approx. 27120 seconds, a diffusivity of  $5.0 \times 10^{-8}$  cm<sup>2</sup>/sec. can be calculated.

These results correspond well with the values for permeability of  $3 \times 10^{-8}$  cm<sup>3</sup>/cm<sup>2</sup> sec. Bar at 70 °C substantiated by Shell Chemicals.

### 20 Example 3

By use of the same equipment as mentioned in example 1, a polymer having the same composition but of a higher molecular weight was extruded. Use was made of a so-called Carilon CXP 1106 from Shell Chemicals.

25 Extrusion was effected on a 15.25 cm (6 inches) metal carcass having a 15.25 cm inner diameter. The temperature in the extruder was set to 250 °C in the initial zone, 230 °C in the subsequent zones, and 235 °C in the major part of the heating zones of the crosshead tool, except  
30 for the last zones where the metal carcass is in close contact with the crosshead and where the temperature is

set to 250 °C. Extrusion is effected at a thickness of approx. 7 mm.

Extrusion effected at a rate of 0.5 meter/min. and for a period of 2 hours produced a barrier layer of a  
5 satisfactory quality lengths of more than 50 meters.

The process was stable without any changes in pressure, temperature and power consumption, which indicates that it is possible to effect a continuous extrusion in a stable process for several days. The workpiece could be  
10 wound up and treated like corresponding semi-manufactured products of other materials.

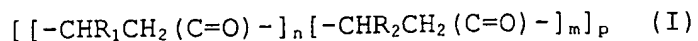
In samples of said liner, cut in chop form of a thickness of approx. 2.0 mm in longitudinal direction, as provided by the ASTM 638 standard, a tensile test performed at 50  
15 mm/min at 23 °C measured a tensile strength of 50.8 MPa and an elongation after fracture of 340-380%.

This corresponds well with the technical documentation produced by Shell Chemicals, which mentions a tensile strength of 63 MPa and an elongation after fracture of  
20 230 to 300% at 23 °C (presumably samples produced by injection moulding).

Thus, the above extrusion does not reduce the stiffness of the material.

## C L A I M S

1. A flexible, unbonded continuous high-pressure pipe, which pipe is composed of several layers comprising at least one inner barrier layer, at least one tubular liquid-permeable reinforcement layer surrounding the barrier layer and a tubular outer sheath surrounding the tubular reinforcement layer(s), at least one of the liquid-impervious barrier layers being provided by continuous extrusion of a single-phase aliphatic polyketone polymer, which polymer comprises at least 80% by volume of an aliphatic polyketone having the formula (I)



where  $R_1$  og  $R_2$  are mutually different and independently mean hydrogen or an alkyl group, preferably methyl-, ethyl-, propyl-, pentyl-, or heptyl-, and  $n + m = 1$ , where  $n$  is preferably less than 0.5, in particular preferably between 0.02 and 0.08, and  $p$  is an integer, preferably an integer between 500 and 5000, and where the two comonomers are randomly distributed or blocked.

2. The flexible, unbonded pipe according to claim 1, characterized in having a length of at least 50 meters.

3. The flexible, unbonded pipe according to claim 1 or 2, characterized in that the liquid-impervious barrier layer consists of a single-phase aliphatic polyketone polymer comprising at least 90% by volume, preferably at least 95% by volume, of an aliphatic polyketone having the formula (I).

4. The flexible, unbonded pipe according to claims 1 to 3, characterized in that  $R_1$  is  $\text{CH}_3$  and  $R_2$  is H.
- 5 3. The flexible, unbonded pipe according to claims 1 to 3, characterized in that  $n = 0$ , and  $R_2$  is preferably H.
6. The flexible, unbonded pipe according to claims 1 to 3, characterized in that  $R_1$  is  $\text{CH}_3$ ,  $R_2$  is H, and  $n$  is less than 0.10, preferably between 0.02 and 10 0.08.
7. The flexible, unbonded pipe according to claims 1 to 3, characterized in that  $R_1$  is alkyl,  $R_2$  is H, and  $n$  is less than 0.10
8. The flexible, unbonded pipe according to claims 1 to 15 7, characterized in that the pipe further comprises a tubular inner metal cylinder.
9. The flexible, unbonded pipe according to claim 8, characterized in that the tubular inner metal cylinder is composed of a liquid permeable metal 20 carcass.
10. The flexible, unbonded pipe according to claims 8 to 9, characterized in that the tubular inner metal cylinder preferably is made from stainless steel.
11. The flexible, unbonded pipe according to claims 8 to 25 10, characterized in that the liquid-impervious barrier layer is extruded directly onto the exterior surface of the tubular inner metal cylinder, preferably onto one or more windings on said tubular inner metal cylinder.



12. The flexible, unbonded pipe according to claims 1 to 11, characterized in that the inner barrier layer has a thickness of 5 to 12 mm, preferably from 6 to 10 mm.
- 5 13. The flexible, unbonded pipe according to claims 1 to 12, characterized in that the inner diameter of the pipe, measured as the inner diameter of the tubular inner metal cylinder, is at least 5 cm, preferably at least 15 cm.
- 10 14. A method of producing a flexible, unbonded high-pressure pipe according to claim 1 comprising the steps of
- optionally providing a tubular inner metal cylinder
  - providing at least one liquid-impervious barrier layer
  - 15 by continuous extrusion
  - reinforcing the pipe with at least one layer of metal band
  - providing a liquid-impervious, tubular outer sheath
  - assembling the tubular parts provided and sealing said
  - 20 parts at each end to form an endfitting,
- wherein the liquid-impervious barrier layer is provided by continuous extrusion of a single-phase aliphatic polyketone polymer comprising at least 80% by volume of an aliphatic polyketone polymer of the formula (I)
- 25 
$$[[-\text{CHR}_1\text{CH}_2(\text{C}=\text{O})-]_n[-\text{CHR}_2\text{CH}_2(\text{C}=\text{O})-]_m]_p \quad (\text{I})$$
- where  $R_1$  og  $R_2$  are mutually different and independently mean hydrogen or an alkyl group, preferably methyl-, ethyl-, propyl-, pentyl-, or heptyl-, and  $n + m = 1$ ,

where  $n$  is preferably less than 0.5, in particular preferably between 0.02 and 0.08, and  $p$  is an integer, preferably an integer between 500 and 5000, and where the two comonomers are randomly distributed or blocked,

- 5 wherein the extrusion equipment used comprises a distributor, a crosshead, and an extruder, and

wherein the mean temperature of the polymer in the distributor and in the crosshead does not exceed the melting point of the polymer by more than 15 °C, and the  
10 mean retention time of the polymer in the extruder, distributor and crosshead does not exceed 20 minutes, while the local temperature of the polymer does not exceed the melting point of the polymer by more than 35 °C for a maximum period of 5 minutes.

- 15 15. The method according to claim 14, characterized in that the liquid-imperious barrier layer is comprised of a single-phase aliphatic polyketone polymer comprising at least 90% by volume, preferably at least 95% by volume, of an aliphatic polyketone polymer of the  
20 formula (I).

16. The method according to claims 14-15, characterized in that that tubular barrier layer is extruded directly onto a tubular inner metal cylinder, optionally with a winding provided between them.

- 25 17. The method according to claim 16, characterized in that the tubular inner metal cylinder is a metal carcass.

18. The method according to claims 16-17, characterized in that the tubular inner metal cylinder is  
30 made from stainless steel.

19. The method according to claims 14-18, c h a r a c -  
t e r i z e d in that the mean retention time of the  
polymer in the extruder does not exceed 10 minutes.

20. The method according to any of the claims 14-19,  
5 c h a r a c t e r i z e d in that the maximum retention  
time of the polymer does not exceed 3 times the mean  
retention time.

21. The method according to any of the claims 14-20,  
c h a r a c t e r i z e d in that the extruder has at  
10 least 7 heating zones, and the temperature of said  
heating zones is increasing or constant measured from  
inlet to outlet.

22. The method according to any of the claims 14-20,  
c h a r a c t e r i z e d in that the distributor and  
15 crosshead are adjusted by at least 5 heating zones, and  
the temperature of said zones does not deviate by more  
than 5 °C from the temperature set in the extruder.

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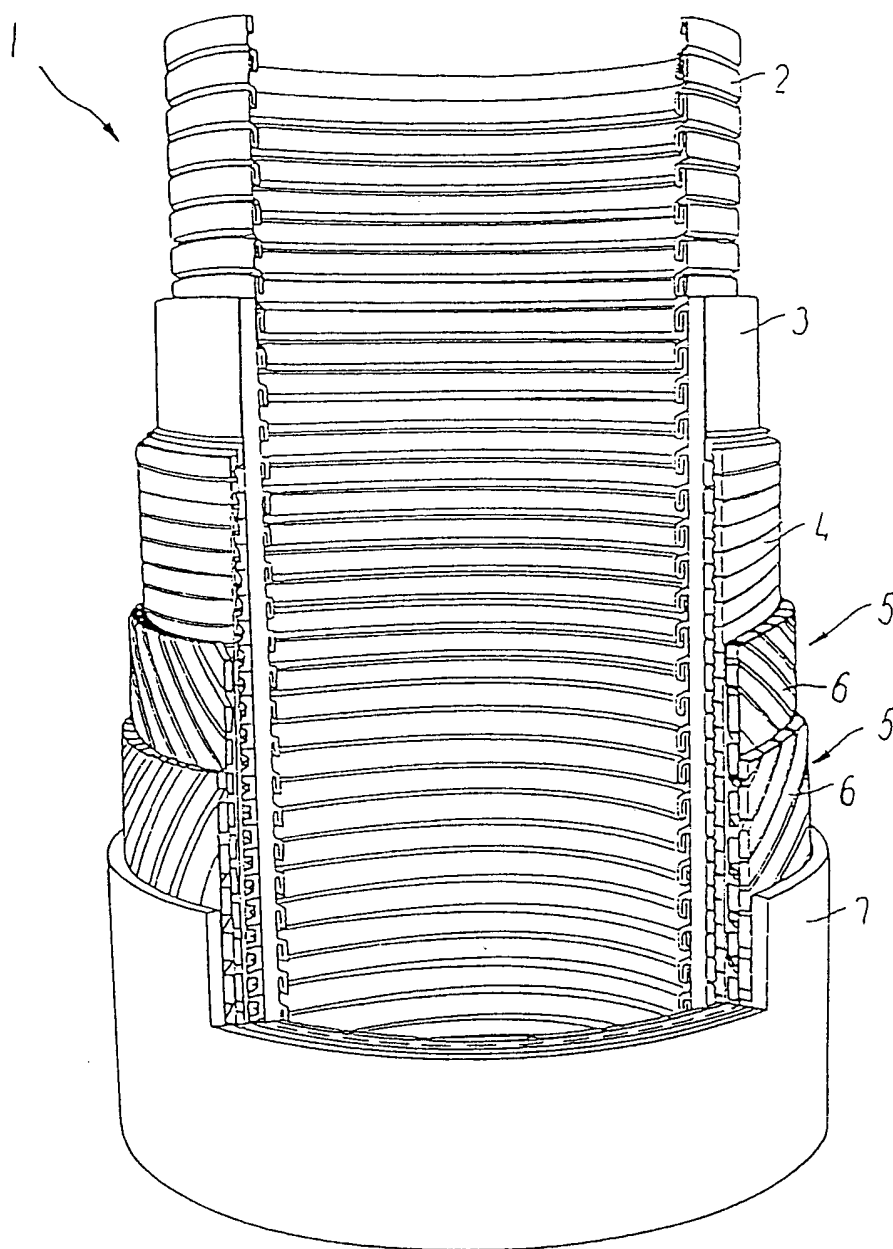


FIG. 1

1  
INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 99/00341

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: F16L 9/12, F16L 11/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: F16L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

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A	NO 165126 B (INSTITUT FRANCAIS DU PETROLE), 17 Sept 1990 (17.09.90) --	1,14
A	FR 2747175 A1 (HUTSCHINSON SOCIETE ANONYME), 10 October 1997 (10.10.97) --	1,14
A	EP 0569101 A1 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.), 10 November 1993 (10.11.93) --	1,14

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents:

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Date of the actual completion of the international search

8 Sept 1999

Date of mailing of the international search report

13 October 1999 (13.10.99)

Name and mailing address of the ISA/  
Swedish Patent Office  
Box 5055, S-102 42 STOCKHOLM  
Facsimile No. +46 8 666 02 86

Authorized officer

Axel Lindhult  
Telephone No. +46 8 782 25 00

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INTERNATIONAL SEARCH REPORT

International application No.  
PCT/DK 99/00341

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

02/08/99

International application No.

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